

Magnetic-Order Induced Spectral-Weight Redistribution in a Triangular Surface System

Gang Li,¹ Philipp Höpfner,² Jörg Schäfer,² Christian Blumenstein,² Sebastian Meyer,² Aaron Bostwick,³ Eli Rotenberg,³ Ralph Claessen,² and Werner Hanke¹

¹*Institut für Theoretische Physik und Astrophysik, Universität Würzburg, 97074 Würzburg, Germany*

²*Physikalisches Institut, Universität Würzburg, 97074 Würzburg, Germany*

³*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

The Sn-induced $\sqrt{3} \times \sqrt{3}$ surface reconstruction on Si(111) has been investigated by material-specific many-body calculations and by angle-resolved photoelectron spectroscopy (ARPES). This triangular surface system in the low adatom coverage regime is governed by rather localized dangling bond orbitals with enhanced electronic correlations and it is prone to exhibit magnetic frustration. We find a rather good overall agreement of the spectral function and its temperature-dependence between theory and experiment. Changes in the ARPES band topology in comparison to the density functional calculations can be explained as a spectral weight redistribution with respect to an additional symmetry which is not due to any geometrical change. This new symmetry corresponds to a magnetic order, which is found to be more complex than the canonical 120° anti-ferromagnetic order on a triangular lattice with nearest-neighbor coupling only.

PACS numbers: 71.10.Fd, 71.27.+a, 71.30.+h

The adatom-covered surfaces of Si(111) and Ge(111) provide an excellent playground to study the competition and cooperation of geometrical frustration and electronic correlations in quasi-two dimensional triangular systems. The deposition of $1/3$ of a monolayer of the group IV elements Pb and Sn renders these surfaces $\sqrt{3} \times \sqrt{3}$ reconstructed [1–3]. These adatoms induce states in the semiconducting band gap, including surface bands which are well separated from the bulk bands. These states are dominated by highly localized dangling bond orbitals, and their narrow band nature leads to enhanced electronic correlations in these systems. Moreover, long-range magnetic ordering is generally suppressed by magnetic frustration inherently contained in such effectively triangular surface lattices [4].

In the α -phase of Pb/Ge(111) [1] and Sn/Ge(111) [2], a transition from a $\sqrt{3} \times \sqrt{3}$ to a 3×3 structure occurs upon cooling, which can be explained within a dynamical fluctuation model [5]. Pb or Sn atoms oscillate vertically at room temperature (RT), but their motions are frozen out at low temperature (LT), leaving two out of three Pb (Sn) atoms per unit cell at a different height than the third one. A similar structural transition might thus be expected to be observed on the surface of Sn/Si(111). However, Sn/Si(111) shows no 3×3 signature in low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) experiments at both RT and LT, down to 6 K [3, 6]. Careful analysis of photoelectron diffraction results further revealed that all Sn adatoms have the same bonding geometry [7].

In addition, in Sn/Si(111) the observed valence-band photoemission spectra show a shadow band at $\bar{\Gamma}_{\sqrt{3}}$ (see Fig. 2 for notations) and an approximate 3×3 periodicity of the overall surface band topology [3, 8]. Also, experimentally a clear conductance dip at the Fermi level

was observed in scanning tunneling spectroscopy at low temperature [7]. The ground state, thus, is believed to be a narrow gap insulator. Calculations based on density functional theory (DFT) in the local-spin density approximation (LSDA) failed to explain both facts, i.e. a *metallic* ground state without backfolded band features at $\bar{\Gamma}_{\sqrt{3}}$ is predicted [9, 10]. The insulating ground state can be explained by the strong electronic correlations favored by the small bandwidth of the Sn/Si(111) surface band. In LSDA + U [4] and more sophisticated local density approximation (LDA) + many-body calculations based on the Hubbard model [11, 12], the ground state is confirmed to be insulating and identified as a narrow gap *Mott insulator*. However, the shadow band feature and the additional band symmetry observed in ARPES have not been explained consistently with respect to all the above mentioned experimental facts. In particular, the inherent spin frustrations contained in Sn/Si(111) further elaborate the issue [12–14] with a remaining lack of knowledge on their interplay with electronic correlations.

In this Letter, we provide a consistent explanation for the surface band topology and the shadow band to originate from electronic correlations rather than from structural aspects. We provide direct evidence from our temperature-dependent calculations that the approximate 3×3 symmetry observed in ARPES is indeed a consequence of magnetic correlations. However, the order associated with it is more complicated than the standard 120° anti-ferromagnetic (AFM) spin-arrangement for triangular surfaces.

Fig. 1 shows our experimental and theoretical situation for the study of the Sn/Si(111) system. Experimentally, clean surfaces were obtained by thermal desorption of the capping oxide at $\approx 1250^\circ\text{C}$ from n-type Si substrates ($\rho < 0.01 \Omega\text{cm}$) resulting in a sharp 7×7 pattern

in LEED. Subsequently, $1/3$ monolayer Sn was deposited on the substrates by electron beam evaporation. After an anneal at $\approx 700^\circ\text{C}$, the Sn/Si(111)- $\sqrt{3} \times \sqrt{3}$ surface reconstruction was verified in high quality by LEED and STM, see Fig. 1(a). Theoretically, we construct a slab with six Si layers and saturate the Si bottom layer by hydrogen atoms. Sn atoms are placed on the top layer at equivalent T_4 lattice sites, see Fig. 1(b). This is in agreement with the atomic structure derived from surface x-ray diffraction [15]. Therefore, we exclude any additional lattice superstructure, e.g., a 3×3 periodicity, in our calculations and expose our system to the electron-electron interaction U only.

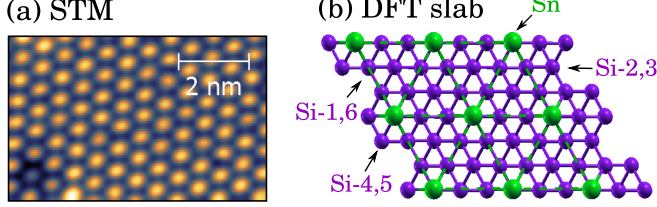


FIG. 1. (a). STM image of the Sn/Si(111) surface at $T = 300\text{ K}$ (bias: -1.0 V ; 0.5 nA). (b). Top view of the DFT-LDA slab consisting of six Si-layers sandwiched between one top Sn-layer and one bottom H-layer (not shown in this figure). Sn atoms align in a plane. A 9-site Sn cluster is used in the DCA calculations (see text).

First, we carry out *ab initio* DFT calculations based on LDA [12], which predict a half-filled metallic ground state of Sn/Si(111), see Fig. 2(a) and (b). This is well in agreement with preceding LDA calculations [9–11]. Next, we project the Sn-related surface band onto the maximally localized Wannier basis and construct a single-band Hubbard model. The dynamical cluster approximation (DCA) [16] is used with the continuous-time quantum Monte Carlo method [17] to solve this model in the paramagnetic phase. We consider a 9-site cluster in our calculations, as shown in Fig. 1(b). The surface Brillouin zone (SBZ) is divided into 9 equal-area sectors. In each of them the electron self-energy becomes a constant, i.e., $\Sigma(k, i\omega_n) \rightarrow \Sigma(K, i\omega_n)$. Our LDA + DCA calculations reported here are the first to examine the spectral weight redistribution in momentum space in the thermodynamic limit for Sn/Si(111). In what follows, we address the theoretical photoemission spectra, which are related in the usual way to the imaginary part of the single-particle Green's function. The latter is calculated following a recipe contained in Ref. [18].

Fig. 2 contains the experimental and theoretical photoemission spectra as a function of position in the SBZ. ARPES experiments were carried out at the electronic structure factory (ESF) endstation of beamline 7.0.1 at the Advanced Light Source (ALS), which provides sample cooling down to 10 K and is equipped with a 6-axis goniometer. Photoelectrons were detected with a Sci-

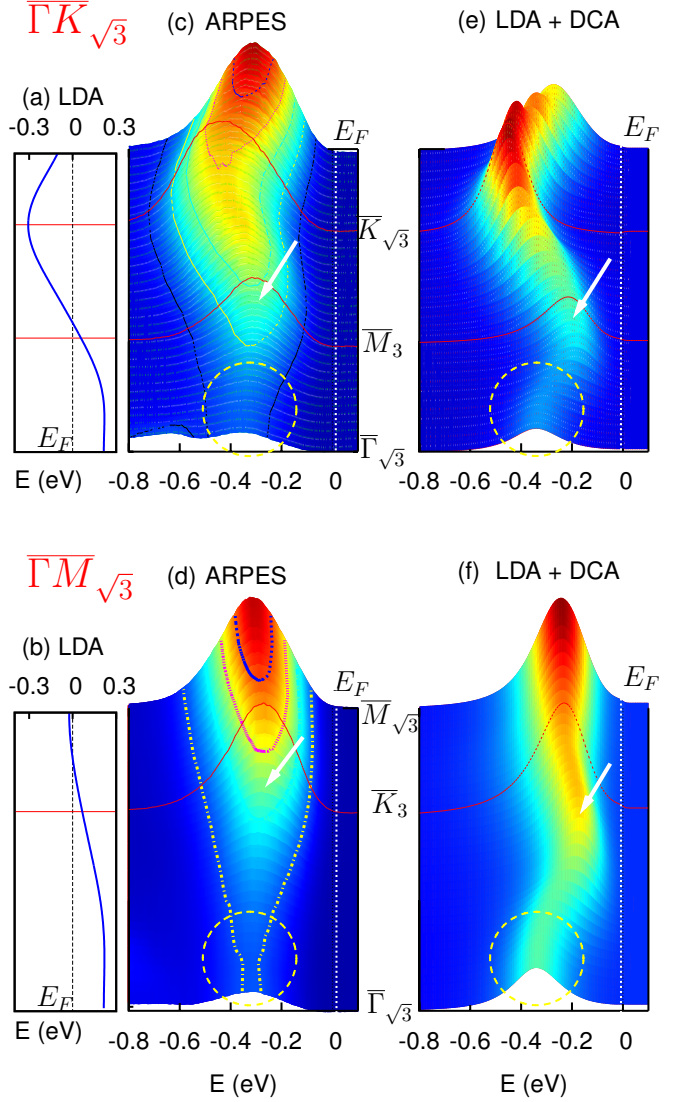


FIG. 2. (a), (b) LDA-derived band structure along the two major high symmetry directions $\Gamma\bar{K}\sqrt{3}$ and $\Gamma\bar{M}\sqrt{3}$ in comparison with (c), (d) corresponding photoemission spectra ($T \approx 60\text{ K}$, $h\nu = 130\text{ eV}$) and (e), (f) the spectral function as obtained from LDA + DCA calculations. In (c) and (d), the contour lines are shown as a guide to the eye. White arrows in (c - f) indicate additional band maxima, which are not present in the LDA-derived band at the same energies. The four yellow circles around $\Gamma\sqrt{3}$ in (c - f) highlight the shadow bands observed in both ARPES and in the LDA + DCA calculations, which are also missing in the LDA-derived band.

enta R4000 spherical analyzer with energy resolution set to 25 meV throughout all measurements. In the theoretical spectra calculations, we set $U \sim 0.66\text{ eV}$, which is slightly above $U_c \approx 0.60\text{ eV}$ for the metal-insulator transition (MIT) in this system [12]. In a related system, i.e. Sn/Ge(111), earlier studies reported two distinct surface

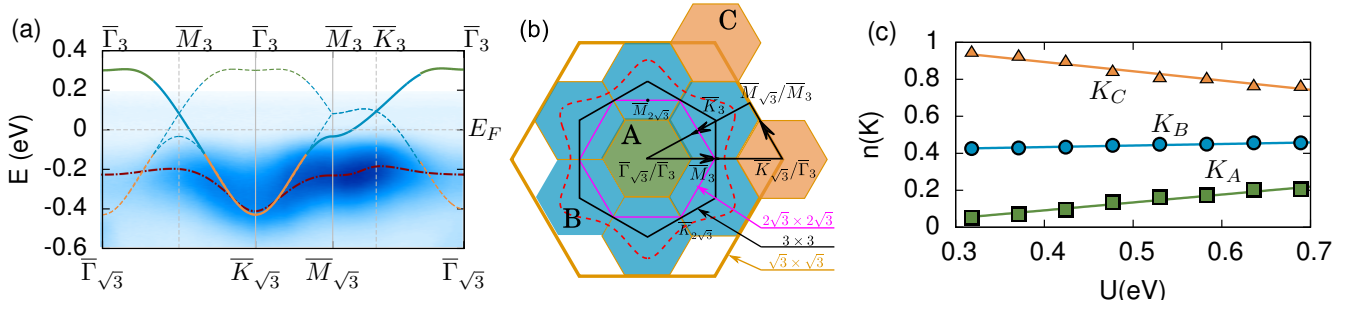


FIG. 3. (a). LDA band structure (solid lines), backfolded LDA bands (dashed lines) with respect to 3×3 SBZ boundaries, and ARPES band map (false color plot) with intensity maximum (red dash-dotted line) indicated as guide to the eye. In order to achieve a better agreement with the experimental band edge at $\bar{K}_{\sqrt{3}}$, we have to scale the LDA-band, which is shown as a solid line in Fig. 3(a), by a factor of 1.3. This scaling effect has essentially been captured by the LDA + DCA calculations in Fig. 2. This factor should not be interpreted as the effective mass of this surface band, since Fermi liquid theory fails to explain the shadow band. (b). The 1st $\sqrt{3} \times \sqrt{3}$ SBZ of the Sn/Si(111) surface, which is divided into three different sectors (A, B, C) in the DCA approximation, see text for more details. The black and violet hexagons correspond to the SBZ of a 3×3 and $2\sqrt{3} \times 2\sqrt{3}$ superstructure. (c). Average particle density in each momentum sector as a function of interaction, reflecting the weight transfer from sector K_C to K_A .

states in ARPES [5, 19]. Sn atoms were believed to stay at two different adsorption sites [20–22] in this system. However, in the Sn/Si(111) surface band, such a splitting is very small at low temperature and even absent at room temperature [3, 8]. We do not want to study such small energy differences in our theoretical spectral function, which contains the uncertainty from the analytical continuation. However, it should be noted that quantum Monte Carlo calculations have shown that strong electron repulsions can further split the lower Hubbard band [23, 24]. Thus, whether or not the two peak structure in that system should be attributed to a geometrical change deserves a more careful study. Moreover, it was shown in a recent theoretical work that electron correlations alone can induce structural transformations in elemental iron [25]. Here, we will not address such additional effects. For Sn/Si(111) we compare ARPES and theory by focusing on the band topology and its k-dependent spectral weight.

Two ARPES k-space line scans along $\bar{\Gamma}\bar{K}_{\sqrt{3}}$ and $\bar{\Gamma}\bar{M}_{\sqrt{3}}$ are shown next to the corresponding LDA + DCA results in Fig. 2(c) to (f). Rather good overall agreement can be detected in this comparison. Along both $\bar{\Gamma}\bar{K}_{\sqrt{3}}$ and $\bar{\Gamma}\bar{M}_{\sqrt{3}}$, we observe a shadow band in ARPES around $\bar{\Gamma}_{\sqrt{3}}$, as indicated by yellow circles in Fig. 2(c) and (d). The evolution of this band clearly shows an *additional band maximum* at a position close to \bar{M}_3 along $\bar{\Gamma}\bar{K}_{\sqrt{3}}$ and in vicinity of \bar{K}_3 along $\bar{\Gamma}\bar{M}_{\sqrt{3}}$ indicated by the white arrows. \bar{M}_3 and \bar{K}_3 are high symmetry points of a 3×3 SBZ. The appearance of the additional band maximum, which is absent in the LDA results in Fig. 2(a) and (b), modifies the spectral dispersion from $\sqrt{3} \times \sqrt{3}$ to an approximate 3×3 symmetry. In the LDA + DCA calculations shown in Fig. 2(e) and (f), both the *shadow band* and its spectral evolution as a function of momentum are

well reproduced. The shadow band is clearly visible in theory and slightly more pronounced than in the experimental spectra. The overall agreement between ARPES and the LDA + DCA calculations, and especially the appearance of this shadow band, represent strong evidence of many-body effects in this system. In contrast, a structural origin is rather unlikely since in our calculations all Sn atoms are located at equivalent lattice sites within the same atomic layer. Thus, the approximate 3×3 symmetry cannot result from any structural change, which is essentially in accordance with the already mentioned absence of a surface-band splitting in the Sn/Si(111) system at low temperatures.

Profeta and Tosatti suggested that the 120° -AFM ordering and consequent folding might be the origin of the shadow band [4]. In what follows, we want to demonstrate that it is very likely that this system is magnetically short range ordered. However, a strict 120° -AFM order cannot fully explain the surface band topology, especially the energy range of the shadow band and the position of the band maximum which is not located exactly at \bar{K}_3 along the $\bar{\Gamma}\bar{M}_{\sqrt{3}}$ direction. According to Profeta and Tosatti, we backfold the original LDA-band into the 1st SBZ with respect to the 3×3 SBZ boundary, which then corresponds to a 120° -AFM order. In Fig. 3(a), the original LDA-band is plotted as a solid line along the $\bar{\Gamma}\bar{K}\bar{M}\bar{\Gamma}_{\sqrt{3}}$ directions, the dashed lines are the folded bands. The high symmetry points of the 3×3 SBZ are labeled as $\bar{\Gamma}_3$, \bar{M}_3 , \bar{K}_3 . Three different colors on the LDA and the backfolded bands are used to indicate different momentum sectors, as those in Fig. 3(b). These three inequivalent momentum sectors are derived from the symmetry preserved in the 9-site cluster DCA calculations, which are labeled as sector A, B and C. The high symmetry points, i.e., $\bar{\Gamma}_{\sqrt{3}}$, $\bar{M}_{\sqrt{3}}$ and $\bar{K}_{\sqrt{3}}$, are contained in sector A, B and C, respectively. The red dashed

line represents the Fermi surface (FS) of the LDA band, which is completely contained in sector B. Evidently, in the 3×3 SBZ a band is located around $\bar{\Gamma}_{\sqrt{3}}$ at $E < 0$, which is obviously back-folded from $\bar{K}_{\sqrt{3}}$, see Fig. 3(a).

First of all, our calculations strongly support the existence of a magnetic order and the consequent band back-folding. In Fig. 3(c), the average particle numbers $n(k)$ at each momentum sector are shown as a function of the interaction U . $n(k)$ was directly calculated in the LDA + DCA. It relates to the spectral function $A(k, E)$ by $n(k) = \int_{-\infty}^{\infty} dE A(k, E) f(E, T)$, where E denotes the energy and $f(E, T)$ the Fermi function. We found qualitatively a different behavior of $n(k)$, when $k \in K_A, K_B$ or K_C . $n(K_A)$ monotonically grows with the increase of the interaction, while $n(K_C)$ behaves exactly the opposite. In contrast, $n(K_B)$ stays almost constant while varying U . In sector B, with the increase of U , the quasiparticle peak at the Fermi level gradually loses its weight until a *charge gap* opens. The constant value of $n(K_B)$, therefore, strongly indicates that the total spectral weight in sector B does not change, however, the spectral weight lost at the quasiparticle peak transfers to the lower and upper Hubbard bands within this sector. The constant value of $n(K_B)$ is a strong indication of the *Mott type* of the MIT. Moreover, an increasing U results in a spectral weight transfer from sector C to sector A. In the $U = 0$ limit, there is no intensity at $\bar{\Gamma}_{\sqrt{3}}$ for energies $E < 0$, giving the almost zero value of $n(K_A)$. For higher values of U , part of the spectral weight around $\bar{K}_{\sqrt{3}}$ transfers to $\bar{\Gamma}_{\sqrt{3}}$, resulting in the increasing/decreasing behaviors of $n(K_A)/n(K_C)$. Thus, what we observe from Fig. 3(b) mainly reflects the spectral weight transfer from $\bar{K}_{\sqrt{3}}$ to $\bar{\Gamma}_{\sqrt{3}}$, which strongly supports the *band back-folding* picture.

However, a strict 3×3 symmetry cannot fully explain the shadow band we observed. A close comparison of ARPES and the folded LDA bands reveals that the shadow band at $\bar{\Gamma}_{\sqrt{3}}$ is not at the same energy as the band at $\bar{K}_{\sqrt{3}}$, as it would be if the magnetic order was 120° -AFM. The shadow band stays at higher energies than that at $\bar{K}_{\sqrt{3}}$. Thus, the magnetic SBZ of Sn/Si(111)- $\sqrt{3} \times \sqrt{3}R30^\circ$ can only be approximate to 3×3 . It reflects that the magnetic order derived from our ARPES and calculations is actually close to but different from the classic 120° -AFM for triangular systems. This is partially due to additional hopping processes inherently contained in Sn/Si(111) as compared to the ideal triangular model with nearest-neighbor hopping only. In our previous study, we found that the inclusion of the next-nearest-neighbor hopping in triangular lattices changes the spin-susceptibility peak-position from near $\bar{K}_{\sqrt{3}}$ to $\bar{M}_{\sqrt{3}}$ in the 1st SBZ which indicates a magnetic order change from 120° -AFM to a *row-wise* (RW) type AFM [12]. This is equivalent to the magnetic ordering in the Mn/Cu(111) surface, which can be effec-

tively described by a triangular Heisenberg model with higher order exchange interactions [26]. The superposition of three equivalent spin arrangements of RW-AFM order, which possess a $2\sqrt{3} \times 2\sqrt{3}$ magnetic SBZ, can further lower the total energy and is thus favored. \bar{M}_3 of the 3×3 SBZ is also a high symmetry point of the $2\sqrt{3} \times 2\sqrt{3}$ SBZ. However, as can be seen from Fig. 3 (b), $\bar{M}_{2\sqrt{3}}$ of $2\sqrt{3} \times 2\sqrt{3}$ is close to but different from \bar{K}_3 of the 3×3 SBZ, which essentially explains the agreement of the band maximum position with \bar{M}_3 along $\bar{\Gamma}\bar{M}_{\sqrt{3}}$ and the discrepancy with \bar{K}_3 along $\bar{\Gamma}\bar{K}_3$. The current surface-band topology study and the spin susceptibility calculations in our previous work [12] coincide with each other, and both point at the magnetic order to be of RW-AFM type. To this end, a spin symmetry-broken many-body calculation and a spin-resolved STM study are highly desirable for further understanding of this adatom system.

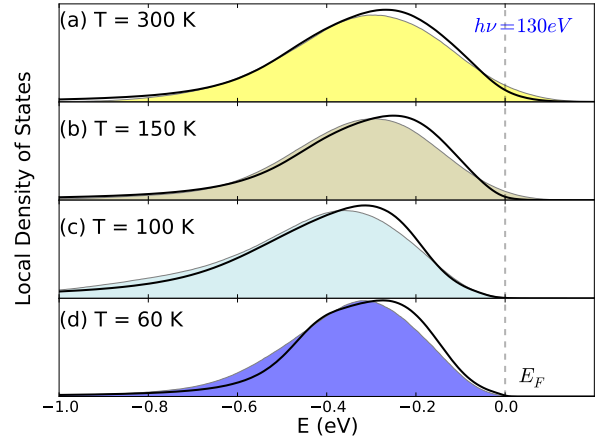


FIG. 4. Comparison of the angle-integrated ARPES spectra (color filled area) with the local density of states calculated from the LDA + DCA at $U = 0.66$ eV (solid black lines) for different temperatures.

In Fig. 4, we show a comparison of the temperature dependent angle-integrated photoemission spectra with the local density of states (LDOS) calculated from the LDA + DCA. The experimental curves are obtained by integrating the ARPES results along the $\bar{\Gamma}_{\sqrt{3}} \rightarrow \bar{M}_{\sqrt{3}} \rightarrow \bar{K}_{\sqrt{3}} \rightarrow \bar{\Gamma}_{\sqrt{3}}$ directions. Experimentally, we observe a MIT between $T = 100$ K and 150 K. The angle-integrated spectral weight at the Fermi level becomes nonzero with increasing temperature. This is in agreement with the many-body description of a Mott MIT. On the other hand, higher temperature has almost no effect on the spectra far away from E_F . We find a marginal change on the spectra for energies below -0.6 eV. In contrast, for increasing temperatures spectral weight is transferred towards the Fermi level, driving this surface system from insulator to metal. Theoretically, for $U = 0.66$ eV we obtain an overall good agreement with the experiments for different temperatures. At all temperatures represented

in Fig. 4, the part of the LDOS close to the Fermi level coincides well with its experimental counterpart.

In summary, we have shown that the key features of a triangular adatom system, realized by the Sn/Si(111)- $\sqrt{3} \times \sqrt{3}R30^\circ$ surface, can be qualitatively explained by strong electronic correlations. By assuming a planar configuration of the Sn atoms, we find a good overall agreement between experiment and the LDA + DCA calculations. A temperature dependent MIT is found, which closely coincides with the Mott description for this surface system. We find strong evidence for a spectral weight transfer from the momentum region around $\bar{K}_{\sqrt{3}}$ to $\bar{\Gamma}_{\sqrt{3}}$, indicating the existence of a magnetic order in this system. The additional symmetry observed in ARPES can then be understood as a band back-folding with respect to a new magnetic ordering. This should stimulate further studies on the magnetic properties of this and related systems.

This work is financially supported by the Deutsche Forschungsgemeinschaft under grant FOR 1162.

-
- [1] J. M. Carpinelli, H. H. Weitering, E. W. Plummer, and R. Stumpf, *Nature (London)* **381**, 398 (1996).
 - [2] J. M. Carpinelli, H. H. Weitering, M. Bartkowiak, R. Stumpf, and E. W. Plummer, *Phys. Rev. Lett.* **79**, 2859 (1997).
 - [3] R. I. G. Uhrberg, H. M. Zhang, T. Balasubramanian, S. T. Jemander, N. Lin, and G. V. Hansson, *Phys. Rev. B* **62**, 8082 (2000).
 - [4] G. Profeta and E. Tosatti, *Phys. Rev. Lett.* **98**, 086401 (2007).
 - [5] J. Avila, A. Mascaraque, E. G. Michel, M. C. Asensio, G. LeLay, J. Ortega, R. Pérez, and F. Flores, *Phys. Rev. Lett.* **82**, 442 (1999).
 - [6] H. Morikawa, I. Matsuda, and S. Hasegawa, *Phys. Rev. B* **65**, 201308 (2002).
 - [7] S. Modesti, L. Petaccia, G. Ceballos, I. Vobornik, G. Panaccione, G. Rossi, L. Ottaviano, R. Larciprete, S. Lizzit, and A. Goldoni, *Phys. Rev. Lett.* **98**, 126401 (2007).
 - [8] J. Lobo, A. Tejada, A. Mugarza, and E. G. Michel, *Phys. Rev. B* **68**, 235332 (2003).
 - [9] G. Santoro, S. Scandolo, and E. Tosatti, *Phys. Rev. B* **59**, 1891 (1999).
 - [10] G. Profeta, A. Continenza, L. Ottaviano, W. Mannstadt, and A. J. Freeman, *Phys. Rev. B* **62**, 1556 (2000).
 - [11] S. Schuwalow, D. Grieger, and F. Lechermann, *Phys. Rev. B* **82**, 035116 (2010).
 - [12] G. Li, M. Laubach, A. Fleszar, and W. Hanke, *Phys. Rev. B(R)* **83**, 041104 (2011).
 - [13] H. Morita, S. Watanabe, and M. Imada, *Journal of the Physical Society of Japan* **71**, 2109 (2002).
 - [14] D. A. Huse and V. Elser, *Phys. Rev. Lett.* **60**, 2531 (1988).
 - [15] K. Conway, J. Macdonald, C. Norris, E. Vlieg, and J. van der Veen, *Surface Science* **215**, 555 (1989).
 - [16] T. Maier, M. Jarrell, T. Pruschke, and M. H. Hettler, *Rev. Mod. Phys.* **77**, 1027 (2005).
 - [17] A. N. Rubtsov, V. V. Savkin, and A. I. Lichtenstein, *Phys. Rev. B* **72**, 035122 (2005).
 - [18] M. Ferrero, P. S. Cornaglia, L. D. Leo, O. Parcollet, G. Kotliar, and A. Georges, *EPL (Europhysics Letters)* **85**, 57009 (2009).
 - [19] R. I. G. Uhrberg and T. Balasubramanian, *Phys. Rev. Lett.* **81**, 2108 (1998).
 - [20] R. Pérez, J. Ortega, and F. Flores, *Phys. Rev. Lett.* **86**, 4891 (2001).
 - [21] R. Cortés, A. Tejada, J. Lobo, C. Didiot, B. Kierren, D. Malterre, E. G. Michel, and A. Mascaraque, *Phys. Rev. Lett.* **96**, 126103 (2006).
 - [22] S. Colonna, F. Ronci, A. Cricenti, and G. Le Lay, *Phys. Rev. Lett.* **101**, 186102 (2008).
 - [23] C. Gröber, R. Eder, and W. Hanke, *Phys. Rev. B* **62**, 4336 (2000).
 - [24] R. Preuss, W. Hanke, C. Gröber, and H. G. Evertz, *Phys. Rev. Lett.* **79**, 1122 (1997).
 - [25] I. Leonov, A. I. Poteryaev, V. I. Anisimov, and D. Vollhardt, *ArXiv e-prints* (2011), [arXiv:1110.0439 \[cond-mat.mtrl-sci\]](https://arxiv.org/abs/1110.0439).
 - [26] P. Kurz, G. Bihlmayer, K. Hirai, and S. Blügel, *Phys. Rev. Lett.* **86**, 1106 (2001).